

ICP - Mass Spectrometry

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Analysis of Petroleum Products According to ASTM Method D8110-17 Using the NexION 2200 ICP-MS

Introduction

The ASTM method D8110-17 titled "Standard Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass

Spectrometry (ICP-MS)"¹ describes a procedure for the determination of a few trace elements in light and middle distillate petroleum products using ICP-MS. Traditionally, such analysis was performed by inductively coupled plasma optical emission spectroscopy (ICP-OES) and atomic absorption spectroscopy (AAS), but specifications for some elements have changed and technology with better detection limits, such as ICP-MS, is now required.²

Contaminants in feedstock can harm refinery processes. Those in petroleum products can compromise the quality of fuels, causing premature breakdown of mechanical equipment, poison catalysts, and impact performance of the final products, such as various chemicals, plastics, and synthetic materials. They also may have harmful effects on the environment when discharged.

Light petroleum distillate products, such as naphtha and jet fuel, with low boiling points are usually diluted in a less volatile solvent for analysis, while middle products, such as kerosene, can be analyzed directly.

There are certain challenges in analyzing petroleum products. Volatile samples can destabilize or even extinguish the plasma. Also, carbon may build up in the sample introduction system and deposit on the interface cones. In addition, carbon-based spectral interferences on several analytes of interest can lead to false analytical results.

Fortunately, these challenges can be easily overcome with PerkinElmer's NexION® ICP-MS portfolio. This work presents the analysis of petroleum products according to ASTM D8110-17 using the NexION 2200 ICP-MS.³ The NexION 2200, featuring a free-running 34-MHz RF generator, delivers fast impedance matching to rapidly adjust to changing sample matrices, while the wide-aperture cones of the Triple Cone Interface (TCI) with OmniRing™ technology⁴ offer unparalleled resistance to clogging, and most importantly, enhanced sensitivity. Furthermore, the ability to use pure reaction gases, such as NH₃, in the quadrupole-based Universal Cell (UCT)⁵ is instrumental for removing spectral interferences.

Experimental

Sample and Standard Preparation

For this study, three commercial petroleum products were analyzed representing light naphthas – Odorless Paint Thinner “Mona Lisa”, 100% Pure Odorless Mineral Spirit “Gamsol” and Industrial Paint Thinner “Varsol”. Before analysis, these samples were diluted w/w 1:10 with V-Solv™ ICP Solvent (PerkinElmer, Shelton, Connecticut, USA).

V-Solv ICP Solvent is a proprietary solvent that is used for diluting oil and other organic liquids for analysis by ICP and ICP-MS, offering several advantages over conventional kerosene, xylene and other commercial solvents: very high purity, stable dilutions of oil standards and organic samples and extremely low odor and toxicity.

As a method accuracy check, a diluted NIST Standard Reference Material 1634c, Trace Elements in Fuel Oil, was used.

The calibration standards were prepared from the V-26 Wear Metal Standard (PerkinElmer) by dilution in V-Solv. The diluted Wear Metal Standards V-21+K (PerkinElmer) was used as a calibration verification solution. A diluted Co Single Element in Hydrocarbon Oil Standard (PerkinElmer) was spiked into the V-Solv blank, standards and samples, as an internal standard.

Instrumentation and Parameters

In this application note, the PerkinElmer NexION 2200 ICP-MS, a single-analyzer-quadrupole system with three-quad design described in detail in the NexION 2200 interactive brochure, was employed. The combination of its novel, second-generation Triple Cone Interface (TCI) with OmniRing technology, patented plasma generator, and LumiCoil™ RF coil enhance the instrument's analytical performance and sensitivity, as well as reliability. The balanced and free-running RF generator, designed explicitly for ICP-MS applications, delivers improved robustness, high efficiency, and a wide power range. It ensures stability while running organic solvents. The proprietary quadrupole-based Universal Cell (UCT), pressurized with 100% pure ammonia, through predictable and repeatable reactions provides superior spectral interference removal, improving method detection limits (MDLs) and reliability of results. Instrumental parameters are listed in Table 1.

Table 1. NexION 2200 ICP-MS Instrumental Parameters.

Parameter	Description/Value
Sample Uptake Rate	~200 µL/min
Nebulizer	Glass with PFA 0.25 mm i.d. probe (self-aspirating)
Spray Chamber	Glass Cyclonic
O ₂ Port	O ₂ , 6% of nebulizer flow
PC3+, Peltier Cooler	-5 °C
Torch	Quartz, demountable for organics
Injector	Quartz 1.0 mm
RF Power	1600 W
Cones	Pt-tip Sampler and Skimmer, Ni Hyper-Skimmer with OmniRing
Acquisition Modes	Standard and Reaction with NH ₃ (100%)
Integration Time/Isotope	0.5 sec

Samples were delivered to the system via a self-aspiration PFA probe to avoid potential problems with peristaltic pump stretching or even deterioration during long hours of operation. The MEINHARD® glass nebulizer aspirated samples at a rate of 200 µL/min. The nebulizer flow was optimized for the best sensitivity and lowered slightly to accommodate the O₂ addition (via a spray chamber port) that prevents carbon from building up on the cones. Oxygen flow was 6% of the total nebulizer gas flow. The cyclonic spray chamber was chilled to -5 °C to lower the solvent vapor entering the plasma.

When analyzing organic solvents, it is preferred to run a higher plasma gas flow, around 18 L/min, compared with the aqueous solution analyzed at 15-16 L/min. It helps cooling the torch and stabilizing plasma while volatile samples are introduced.

Reaction mode with 100% pure NH₃ is the most effective way of removing argon, oxygen, nitrogen and carbon-based spectral interferences (listed in Table 2) by changing them into atoms or ions of a different mass or by creating a cluster ion with an analyte (Mass Shift) at a higher mass. Some elements without spectral interferences are measured in Standard mode without any gases entering the cell.

Table 2. Potential Spectral Interferences from Carbon Species.

Mass	Interference	Analyte
24-26	C ₂ , CN	Mg
27	CN, CNH	Al
28	CO	Si
31	COH	P
52-53	ArC	Cr

Results and Discussion

The ASTM method D8110-17 has specific requirements regarding calibration, check standards, internal standards, QC samples, MDLs, precision, repeatability and reproducibility. We have addressed these requirements through several tests. The method listed Al, Ca, Cu, Fe, Pb, Mg and K as elements to be analyzed for trace contaminants in distillate products, however, a few other elements that can be potential contaminants were added to our tests.

Calibration Curves

Three calibration standards (10, 20 and 40 ng/g) were prepared from the S-26 Wear Metal Standard by dilution in V-Solv. The V-Solv blank and the standards were spiked with Co as an internal standard to the final concentration of 10 ng/g. The calibration curves for the elements listed in the ASTM method are shown in Figure 1, all having correlation coefficients > 0.9999.

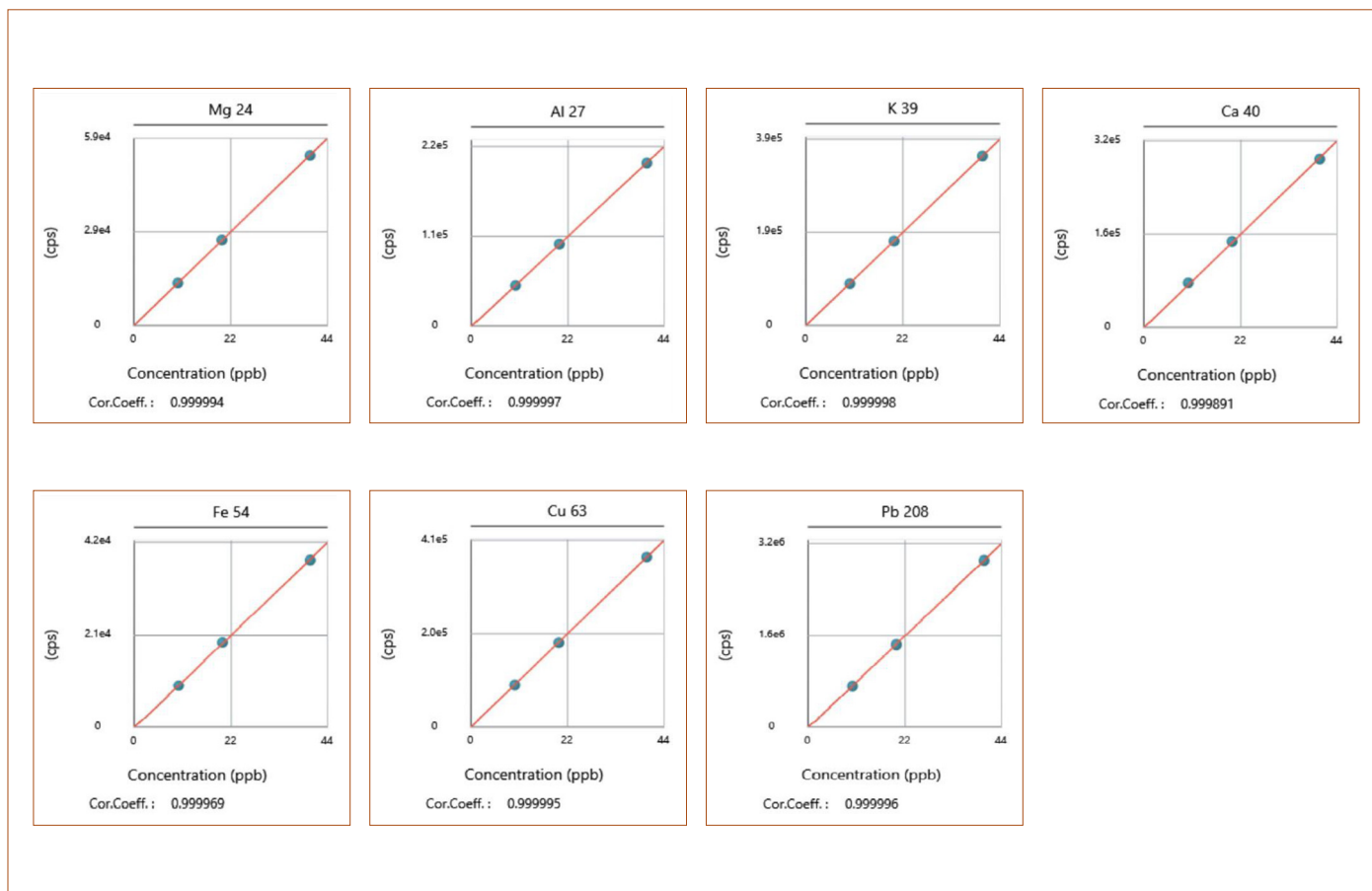


Figure 1. Calibration curves for seven analytes listed in ASTM D8110-17 method.

Method Detection Limits

According to ASTM D8110-17, method detection limits have to be determined annually or whenever a significant change in background or instrument response is expected, using the following formula:

$$\text{MDL} = (t) \times (s)$$

where:

- t = students' t value for a 99% confidence level and with $n-1$ degrees of freedom ($t = 3.14$ for seven replicates)
- s = standard deviation of the replicate analyses

A V-Solv blank spiked with the Co internal standard was measured seven times for the seven method-required elements plus 12 others. The MDLs are listed in Table 3 along with the cell mode for each analyte. MDLs reflect not only the capabilities of the instrumentation, but also the cleanliness of the chemicals used. The Fe MDL was measured at mass 54 and 56. Even though the result on mass 56 was better, mass 54 was used for further analysis to avoid a possible interference from CaO.

When analyzing diluted petroleum products, the dilution factor has to be incorporated in the calculations of MDLs.

Table 3. MDL Results for ASTM Method Elements (in bold) and 12 others.

Analyte	Cell Mode	MDL (ng/g)
Na 23	Standard	0.01
Mg 24	Reaction NH ₃	0.004
Al 27	Reaction NH ₃	0.004
K 39	Reaction NH ₃	0.03
Ca 40	Reaction NH ₃	0.008
Ti 48/131	Reaction NH ₃	0.007
V 51	Reaction NH ₃	0.0003
Cr 52	Reaction NH ₃	0.003
Fe 54	Reaction NH ₃	0.03
Mn 55	Reaction NH ₃	0.0007
Fe 56	Reaction NH ₃	0.01
Ni 60	Reaction NH ₃	0.02
Cu 63	Reaction NH ₃	0.004
Zn 66	Reaction NH ₃	0.03
Mo 95	Standard	0.0005
Ag 107	Standard	0.0006
Cd 111	Standard	0.0007
Sn 118	Reaction NH ₃	0.002
Ba 138	Standard	0.0001
Pb 208+206+207	Standard	0.0002

Validation of Method Analysis

The NIST SRM 1634c, Trace Elements in Fuel Oil, was used for the method validation. The SRM was diluted 1000 times with V-Solv to measure values within the range of the calibration curves. Only Ni and V were certified in this standard. A small concentration of Co does not exclude from using it as an internal standard due to a relatively high Co concentration spiked into all blanks, standards and samples. Table 4 shows excellent recoveries for both elements within $\pm 1\%$.

Table 4. Recoveries of V and Ni in NIST SRM 1634c.

Analyte	Certified Values (mg/kg)	Measured Values (mg/kg)	Recovery (%)
V 51	28.19 \pm 0.40	28.07	99.6
Ni 60	17.54 \pm 0.21	17.67	100.7

QC Results

After the calibration was performed, a second source standard, diluted V-21+K, was analyzed as a QC to verify if the results were in agreement with the $\pm 10\%$ control limit. The correlation was very good, within $\pm 4\%$ for all tested elements.

Table 5. QC - Initial Verification.

Analyte	Expected Values (mg/kg)	Measured Values (mg/kg)	Recovery (%)
Na 23	20	19.38	96.9
Mg 24	20	19.77	98.8
Al 27	20	19.92	99.6
K 39	20	20.55	102.8
Ca 40	20	20.30	101.5
Ti 48/131	20	20.19	101.0
V 51	20	19.70	98.5
Cr 52	20	19.70	98.5
Fe 54	20	20.59	102.9
Mn 55	20	19.71	98.5
Ni 60	20	19.54	97.7
Cu 63	20	19.67	98.3
Zn 66	20	19.79	99.0
Mo 95	20	19.94	99.7
Ag 107	20	19.64	98.2
Cd 111	20	19.78	98.9
Sn 118	20	19.84	99.2
Ba 138	20	19.26	96.3
Pb 208+206+207	20	19.62	98.1

The QC standard was also analyzed every 5 samples (small batches) for a 4-hour run during which several naphtha samples spiked with 2 ppb mixed-element standard were analyzed. In Figure 2, the plot of the QC results is shown, demonstrating excellent stability of the system.

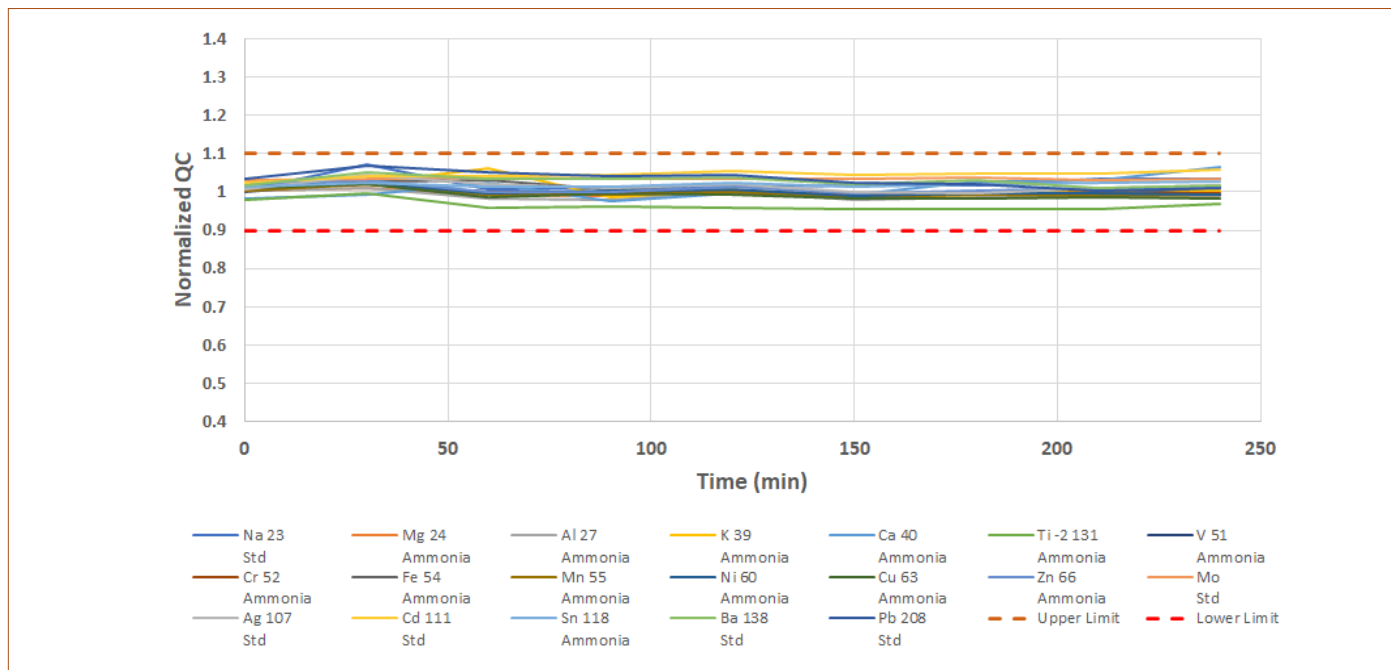


Figure 2. QC analyzed every 5 samples during 4-hour run.

Different viscosities of samples can change the aspiration rate of samples; therefore, one or multiple internal standards are added to samples, standards, and blanks to compensate for that as well as to correct for any potential drift. The ASTM method requires that the internal standard counts should be within 50% to 150% of the calibration blank. In our method, Co was used as the internal standard spiked at the concentration of 10 µg/g and measured in Standard and Reaction modes with two flows of NH₃. Figure 3 shows the internal standard response during a 4-hour analysis of naphtha samples. Naphthas of slightly different viscosity were analyzed, but the internal standard response did not change more than ± 10%.

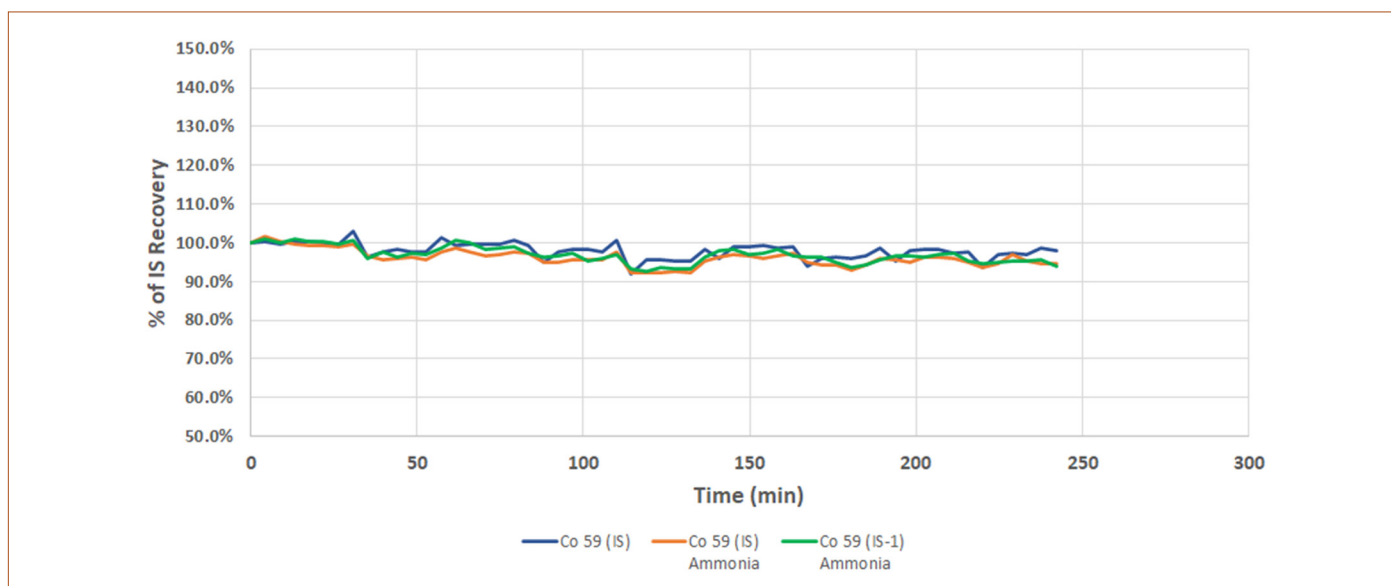


Figure 3. Internal standard response during 4-hour analysis of naphtha samples.

Another test mandated by the ASTM method is a measurement of precision characterized by the Repeatability Limit (r) that is for each of seven elements according to the formulas given in the method. Two separate measurements were carried out on the same naphtha sample spiked with 2 ng/g level. The repeatability results are summarized in Table 6, showing excellent agreement between two measurements.

Table 6. Precision of Analysis at 2 ng/g Spike Level in the Naphtha Sample.

Analyte	Concentration of Spike (ng/g)	ASTM Repeatability Calculated at 2 ng/g Level	1st Measurement (ng/g)	2nd Measurement (ng/g)	Difference Between Two Measurements (ng/g)	Difference Between Two Measurements (%)
Mg	2	1.03	2.03	2.11	0.08	3.90
Al	2	1.05	2.06	2.11	0.05	2.40
K	2	0.39	1.85	1.93	0.08	4.20
Ca	2	0.89	2.06	2.13	0.07	3.30
Fe	2	0.65	2.05	2.07	0.02	1.00
Cu	2	1.86	1.98	2.05	0.07	3.50
Pb	2	1.54	2.11	2.16	0.05	2.30

Analytical Results

Undiluted kerosene (laboratory-grade) and three different commercial light petroleum products (diluted 1:10) were analyzed as samples. The results, summarized in Table 7, show very low levels of contaminants in these commodities.

Table 7. Summary of Analysis of Four Petroleum Products in ng/g.

Analyte	Kerosene Undiluted (ng/g)	Artistic Paint Thinner 10x Diluted (ng/g)	Industrial Paint Thinner 10x Diluted (ng/g)	Mineral Spirit 10x Diluted (ng/g)
Na 23	< MDL	0.200	< MDL	< MDL
Mg 24	0.020	< MDL	< MDL	< MDL
Al 27	0.012	0.014	< MDL	< MDL
K 39	< MDL	< MDL	< MDL	< MDL
Ca 40	0.163	0.315	0.070	< MDL
Ti 48/131	< MDL	< MDL	< MDL	< MDL
V 51	0.003	< MDL	< MDL	< MDL
Cr 52	0.017	< MDL	< MDL	< MDL
Fe 54	< MDL	0.050	< MDL	< MDL
Mn 55	0.089	0.002	< MDL	< MDL
Ni 60	< MDL	< MDL	< MDL	< MDL
Cu 63	< MDL	0.009	< MDL	< MDL
Zn 66	< MDL	< MDL	< MDL	< MDL
Mo 95	< MDL	< MDL	< MDL	< MDL
Ag 107	< MDL	< MDL	< MDL	< MDL
Cd 111	< MDL	< MDL	< MDL	< MDL
Sn 118	< MDL	< MDL	< MDL	< MDL
Ba 138	< MDL	< MDL	< MDL	< MDL
Pb 208+206+207	0.046	< MDL	< MDL	< MDL

Conclusion

The results presented in this application note demonstrate the capability of the NexION 2200 ICP-MS to effectively analyze petroleum distillates according to the ASTM D8110-17 method requirements. The combination of the NexION 2200's unique features, such as the patented SMARTintro™ sample introduction system for organics, LumiCoil load coil, unique 34-MHz RF plasma generator, its second-generation Triple Cone Interface with OmniRing, and a true-quadrupole Universal Cell with dynamic bandpass tuning capabilities, provides the outstanding performance needed for the petroleum industry when analyzing difficult matrices such as distillates of different viscosities and compositions.

References

1. ASTM Method D8110-17, "Standard Test Method for Elemental Analysis of Distillate Products by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)", ASTM International, 2017.
2. Smith S., "Determination of Elements at Sub-ppb Concentrations in Naphtha Mixtures Using the NexION 300/350 ICP-MS", PerkinElmer Application Note, 2014.
3. "NexION 2200 ICP-MS", PerkinElmer Interactive Brochure, 2023.
4. Badiei H. et al., "Advantages of a Novel Interface Design for NexION 2200/5000 ICP-MS", PerkinElmer Technical Note, 2023.

Consumables Used

Component	Part Number
PFA Sample Probe Self-Aspirating 0.25 mm i.d.	N8152512
Demountable Torch for Organics	N8152596
Quartz Injector 1 mm	N8152444
Pt Sampler Cone	W1033614
Pt Skimmer Cone	N8171143
Ni Hyper-Skimmer Cone with OmniRing	N8170140